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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

THE SPEED AND NATURE OF THE REACTION OF BROMINE UPON OXALIC ACID.

By Theodore William Richards and Wilfred Newsome Stull.

Received June 16, 1902.

While the rapid action of bromine upon neutral oxalates is well known, there is a difference of published opinion as to whether or not oxalic acid itself is affected by this halogen in aqueous solution. Wurtz * maintains, without stated authority, that action takes place; while Schönbein † denies this contention, giving brief but inadequate experimental evidence.

The further study of the behavior of these two substances is therefore an obvious need. Moreover, the outcome must be of practical value no matter which statement should prove to be true: for if bromine really acts upon oxalic acid, the speed of the reaction could not but give interesting light as to the disposition of the dissolved acid; while if no action takes place, a ready mode of separating bromine from chlorine (which reacts readily) might be afforded.

A few rough experiments sufficed to show that Wurtz was right and Schönbein wrong. The two substances react slowly upon one another at ordinary room temperatures, and rapidly at high temperatures. Schönbein must have been misled by the fact that at 20° no obvious diminution in the intensity of the color of the mixture takes place in many minutes.

The interest of the problem first centers on the question as to whether the bromine attacks the ion C_2O_4'', the ion HC_2O_4' or the undissociated acid. From the fact that the neutral salt is at once oxidized, the first alternative seemed the most likely; but the hypothesis of ions is not yet on so stable a basis as to permit certain inference.

The oxalic acid used in the following work was purified by recrystallization from hydrochloric acid and water. It contained no residual

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* A. Wurtz, Dict. de Chem., **2**, 671.

† C. F. Schönbein, J. für ppt. Chem. **88**, 484 (1863).

hydrochloric acid. Ten grams of the solid left no residue on evaporation in a platinum dish. The bromine was prepared essentially according to one of the methods of Stas, and was wholly free from all other substances except water.

In order to measure out successive, equal portions of bromine for parallel experiments, an almost saturated solution was kept in a covered bottle, and measured out in a glass-stoppered pipette filled by a siphon, so arranged that the top of the pipette communicated with the bottle.* The cork, the only rubber connection in the apparatus, was protected by soft paraffin, which also served when mixed with a little melted rubber † to lubricate the stopcocks. From this pipette successive portions, differing less than 0.1 per cent in bromine-contents from one another, could be delivered at will. A diagram illustrates this description.

The mode of procedure in the quantitative study of the bromine-oxalic reaction was as follows: —

Into a glass-stoppered bottle of about 65 c.c. capacity a quantity of a solution of oxalic acid was introduced, and into this was run a pipetteful of bromine water. The bottle had been previously adjusted by means of glass pearls, so that its remaining volume was just enough to receive the solutions. The stopper was immediately closed and the bottle was immersed in a thermostat whose temperature was kept constant to within one-tenth of a degree. In order to prevent any leakage, the stopper was lubricated with the rubber-paraffin mixture, which serves to seal hermetically the reacting liquids. The rubber-paraffin mixture was not attacked to any appreciable extent. It is necessary to fill the bottles completely, for, if a free space be left above the solution, bromine vapor will pass into this space and thus cause grave uncertainty in the reacting concentration. After a definite time had elapsed, the bottle was taken from the thermostat, the contents were treated with a solution of potassium iodide, and the liberated iodine was titrated with sodium thiosulphate. The thermostat was covered with a black cloth in order to prevent any reaction between the bromine and water, although, as will be noted later in this paper, this precaution was necessary only when working at higher temperatures.

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* When the solution is delivered from the pipette, air must of course flow in to take its place. If this entering air flows through a bulb-tube containing water and a drop of bromine, the atmosphere of the bottle will remain saturated with bromine without loss to the solution. If this bulb-tube is not provided, the air-ingress must be as distant as possible from the air-tube of the pipette, which should almost touch the liquid in the bottle. This latter arrangement was found in our experiments to answer the requirements of the present work, for a single series may be made with sufficient accuracy. After much air has been admitted, the solution will naturally be somewhat weakened. In each series careful determinations of the strength of the solution were made before the experimenting-bottles were filled; again after filling three bottles, and so on until all were filled, when two final determinations were made.

† This mixture, suggested to one of us by W. Ramsay, has proved itself useful in many exigencies. It is made by melting pure rubber, adding equal weights of hard and of soft paraffin, and evaporating off the more volatile constituents. By varying the proportions any desired consistency may be obtained. It may be filtered when hot through fine cloth to remove accidental infused impurities.

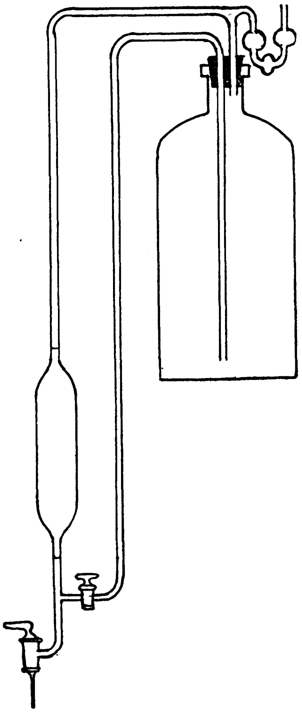

FIGURE 1.

Although there was little probability that the reaction is reversible, yet it was thought advisable to test this point experimentally. For this purpose the rate of reaction of bromine on a solution of oxalic acid in pure water was compared with the rate when bromine acted upon an oxalic solution charged with carbon dioxide. The same quantities of bromine and oxalic acid were present in each case and the time allowed for reaction was one hour. The residual bromine, where carbonic acid was present, was equivalent to 10.29 c.c. of $\frac{n}{10}$ thiosulphate solution. In the absence of carbon dioxide the bromine remaining corresponded to 10.31 c.c. of $\frac{n}{10}$ thiosulphate. The reaction evidently possesses an overwhelming tendency in one direction.

That bromine does not act on water, at ordinary temperature, to any great extent is shown by the following experiment. Three bottles, each containing bromine equivalent to 17.97 c.c. $\frac{n}{10}$ thiosulphate, were tightly stoppered and exposed in the thermostat, at a temperature of 23° C., to the influence of diffused light. At the end of four hours the contents were treated with potassium iodide and the free iodine titrated. The quantities of iodine found corresponded to 17.95 c.c.; 17.96 c.c.; and 17.98 c.c. of $\frac{n}{10}$ thiosulphate. The average 17.96 is essentially equal to the previous value 17.97. For the purposes of this study we may therefore neglect the water-bromine reaction. The probability of an unknown catalytic action called into play in the presence of the oxalic reaction is slight.

I. THE UNCORRECTED TIME CURVE.

In the first series of experiments a large excess of oxalic acid was taken, in order to have its concentration essentially constant. If no disturbing influences, then, entered into the reaction during its progress, the speed at any moment should be essentially proportional to a simple power of the concentration of the bromine. The actual amounts used were 1.496 grams of oxalic acid and 0.1375 gram of bromine made up to 48.3 cubic centimeters. The temperature was 23 °.0.

SERIES I.

No.	Time of Reaction in Minutes.	Weight of Bromine remaining.	Weight of Bromine used.
1	10	.0976	.0399
2	20	.0864	.0511
3	30	.0794	.0581
4	45	.0718	.0657
5	90	.0534	.0841
6	120	.0475	.0900
7	180	.0371	.1004
8	240	.0303	.1072
9	300	.0238	.1137
10	360	.0192	.1183
11	1290	.0013	.1362

Obviously the reaction falls off in speed more rapidly than would have been expected according to any simple interpretation of the results. It was therefore necessary to study the effect of varying, in turn, each condition which might affect the rate of change, in order to find the cause of the anomaly.

II. THE EFFECT OF VARYING THE CONCENTRATION OF OXALIC ACID.

In the following series of experiments the weight of oxalic acid present varied from 0.0587 gram to 4.112 grams in 63.3 cubic centimeters, while the same amount of bromine (0.1601 gram) was originally present in each case. The time of the reaction in each case was 60 minutes.

SERIES II.

No.	Weight of Oxalic Acid in 63 3 c.c. of Solution.	Weight of Br_2 remaining.	Weight of Br_2 used in an Hour.
12	0.0587	.1003	.0598
13	0.1175	.0909	.0692
14	0.2937	0812	.0789
15	0.5873	.0763	.0838
16	0.8810	.0738	.0863
17	1.1746	.0732	.0869
18	1.4682	.0726	.0875
19	1.7619	.0718	.0883
20	2.0556	.0718	.0883
21	2.3462	.0718	.0883
22	2.5700	.0728	.0873
23	4.1120	.0752	.0849

The most evident feature of these results is the fact that the speed of reaction does not increase indefinitely with increasing concentration, but that above a point corresponding to about three per cent of oxalic acid by weight, the speed decreases. For a considerable space, between concentrations containing 0.7 per cent to 4 per cent of oxalic acid, the speed scarcely changes.

Kohlrausch and Holborn* state that the specific conductivity of a 3.5 per cent solution of oxalic acid is 508 ($10\kappa^4_{18}$), while a 7 per cent solution has a conductivity of 783. The comparison of these data with the newly presented fact concerning the speed of the bromine-oxalic acid reaction furnishes new evidence that the C_2O_4'' ion is that which is attacked by the bromine. The following reasoning will make this point clear.

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* Leitvermögen der Electrolyte, p. 157 (1898).

The two following equations represent the two possible equilibria existing side by side in the oxalic solution : —

$$(COO)_2'' + 2H^{\cdot} \leftrightarrows (COOH)_2 \qquad (1)$$

$$(COO)_2H' + H^{\cdot} \leftrightarrows (COOH)_2 \qquad (2)$$

If C = concentration of the ion C_2O_4'', C_1 = concentration of the ion C_2O_4H', C_2 that of the hydrogen ion, and C_3 that of the undissociated acid, the law of "mass-action" demands the following equations of equilibrium : —

$$C\,C_2^2 = \mathrm{K}C_3 \text{ or } C = \frac{\mathrm{K}C_3}{C_2^2} \qquad (3)$$

$$C_1\,C_2 = \mathrm{K}C_3 \text{ or } C_1 = \frac{\mathrm{K}C_3}{C_2} \qquad (4)$$

The concentration of the singly charged oxalic ion will therefore vary inversely as hydrogen concentration, while the double charged ion, $(COO)_2''$, will vary in concentration inversely as the *square* of the hydrogen concentration. It is fair to conclude from this argument, therefore, that the repressing action due to ionized hydrogen would be vastly more effective in eliminating doubly charged ions from the solution than those with a single charge. Therefore we might expect a maximum concentration of C_2O_4'' at a moderate concentration of oxalic acid; and since such a maximum is found in the action of bromine upon the solution, we may suppose this action to take place upon the group C_2O_4''.*

III. THE EFFECT OF FOREIGN SUBSTANCES.

It became now a matter of interest to test the conclusions yet further by adding various foreign substances capable of affecting the ionization of the oxalic acid. Accordingly hydrochloric acid and sodic acetate were used as means of respectively increasing and decreasing the concentration of the hydrogen ion. Each of the following solutions had a volume of 58.3 c.c. and contained 1.496 grams of oxalic acid and 0.1375 gram of bromine. Each was allowed to react for two hours, at 23°.0

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* Mr. F. R. Fraprie has lately shown in this laboratory that while alkaline oxalates readily reduce K_2PtCl_6 to K_2PtCl_4, oxalic acid solutions free from alkali effect this reduction only slowly if at all. This is evidently another case where the *ion* of oxalic acid is the active group.

SERIES III.

No.	Foreign Substance added.	Weight of Bromine used in two Hours.
		gram.
24	None	0.0942
25	0.34 gram hydrochloric acid (HCl)	0.0642
26	3.4 grams hydrochloric acid . . .	0.0029
27	1.0 gram sodic acetate*	0.1128
28	Sodic hydroxide to neutralization .	0.1375 (all)

Thus both substances acted in harmony with the hypothesis, the hydrochloric acid retarding the reaction and the sodic acetate hastening it. It is worthy of note that the retarding effect of the acid increases at a faster rate than its concentration, and taking into account the ionized hydrogen already present, it seems quite possible that the relation may be the quadratic one demanded by theory. Another possible disturbing influence will be pointed out in the sequel.

These observations were verified by repeating the experiments with more dilute solutions, but they need not be recorded, since they furnish no further light upon the problem. Sulphuric acid was found to give a result corresponding to hydrochloric acid. (Exps. 29 to 33.)

It became now a matter of interest to determine if the original time-curve might be corrected for the growing concentration of ionized hydrogen caused by the substitution of bromine as an anion instead of the group C_2O_4''. Preliminary calculation led at once to the conclusion that the slight increase in the ionized hydrogen could by no means account for the rapid loss of speed observed in the first series. It seemed therefore possible that hydrobromic acid might possess some specific effect, and preliminary experiments showed that this was indeed the case to a surprising degree. In two hours 0.0008 mole per litre of hydrobromic acid was found to produce as much depressing effect on the total progress of the reaction as was caused by 0.01 mole of hydrochloric acid.

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* It is not impossible that the acetate ion itself may be slightly attacked by bromine, but considerable action is not likely at the low temperature employed.

Clearly, then, the growing presence of hydrobromic acid must be the cause of the abnormal loss of speed in the original time-curve. But in what manner can the substance effect this change?

The next step was to study in great detail the actual effect of hydrobromic acid of varying strengths.

IV. The Effect of Hydrobromic Acid.

The following series give a basis for more certain conclusions concerning the action of hydrobromic acid. Series IV is merely a repetition of Series I with a somewhat more dilute solution of oxalic acid, Series V contained a few centigrams of hydrobromic acid, and Series VI contained about twice as much of this acid. In each the total volume was 59.30 cubic centimeters, containing at the start 1.495 grams of anhydrous oxalic acid and 0.1536 gram of un-ionized bromine.

As before, the temperature was 23°.0.

SERIES IV.

No.	Time of Reaction in Minutes.	Weight of Bromine remaining.	Weight of Bromine used.
34	10	.1091	.0445
35	20	.0970	.0566
36	30	.0899	.0637
37	45	.0801	.0735
38	60	.0720	.0816
39	120	.0528	.1008
40	180	.0394	.1142
41	240	.0315	.1221
42	300	.0257	.1279
43	360	.0205	.1331
44	320	.0179	.1357

SERIES V.

CONTAINING 0.0675 GRAM OF HBr.

No.	Time of Reaction in Minutes.	Weight of Bromine remaining.	Weight of Bromine used.
45	30	.1249	.0286
46	60	.1080	.0456
47	180	.0741	.0795
48	300	.0536	.1000

SERIES VI.

CONTAINING 0.148 GRAM OF HBr.

No.	Time of Reaction in Minutes.	Weight of Bromine remaining.	Weight of Bromine used.
49	10	.1476	.0060
50	30	.1410	.0126
51	45	.1360	.0176
52	60	.1315	.0221
53	120	.1161	.0375
54	180	.1039	.0497
55	240	.0944	.0592
56	300	.0846	.0690
57	360	.0779	.0757
58	420	.0729	.0807

The results given in these tables are plotted in Figure 2, the bromine present at any time being drawn as ordinate, and the time as abscissa.

In these experiments the amount of oxalic acid (about 2.5 per cent) by weight was so chosen that the concentration of the reacting oxalic molecular species remained essentially constant during the reaction. In

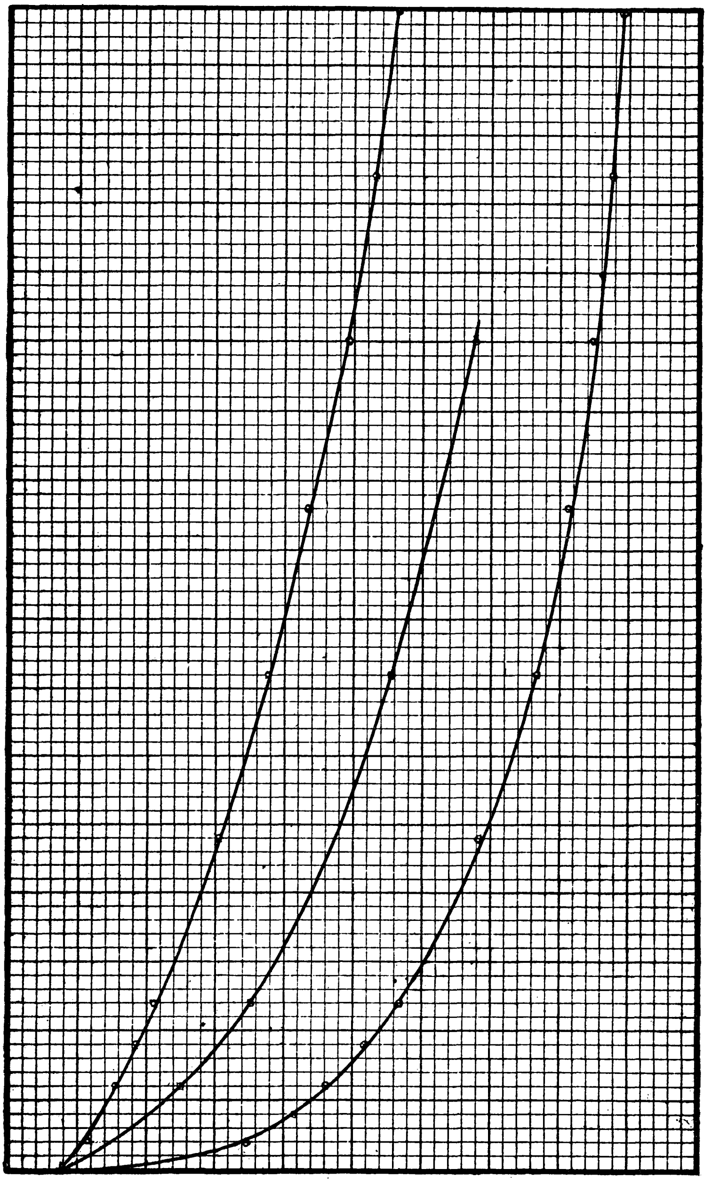

FIGURE 2. Time in minutes is plotted vertically; the weight of bromine remaining is plotted from right to left. The right-hand curve represents Series IV, the middle curve Series V, and the left-hand curve Series VI.

the second series it had been found that the solution might contain any amount from one per cent to five per cent of oxalic acid without any serious variation in the speed.

Hence the peculiarities exhibited by these curves must be due essentially to the presence of varying hydrobromic acid and bromine. The immensely retarding effect of the hydrobromic acid is at once manifest, without further calculation, and evidently the greater the amount of hydrobromic acid, the less rapid is the change of rate as the reaction progresses.

Thus the downward convexity in Series IV is strongly marked, while in the case of Series VI the curve is but slightly bent. The question at once presents itself, — Would the reaction reduce to a monomolecular one, depending upon the concentration of the bromine alone, if the effect of the hydrobromic acid were eliminated? The results in hand furnish the data for answering this question.

An approximate estimate of the speed of reaction at any point in any one of these curves may be obtained by placing a straight-edge tangent to the carefully drawn curve, and noting the ordinate, or bromine value, which corresponds to a given time. This was done quite independently by each of the authors, and the rates thus found agreed essentially with one another. The averages of several series of such readings are recorded in the following table, together with the amounts of hydrobromic acid and the bromine present in each case. The time interval was always reduced to five minutes. The various points are designated by giving the series and the times from the commencement of the reaction, hence they may all be identified upon the diagram, although of course the actual curves from which the readings were taken were drawn upon a much larger scale. The last column contains a function which would be constant if the speed were directly proportional to the concentration of the bromine and inversely proportional to the concentration of the hydrobromic acid. (See page 332.)

In view of the complicated relations concerning the dissociation of the hydrobromic acid, it is surprising that even an approximately constant function could be found. Nevertheless, it is obvious that the requirement of the function $\frac{a\,b}{c}$ is nearly fulfilled. In a case as complicated as this the safest method of solution is to eliminate one variable at a time, not attempting to analyze the reaction at once in a single expression. The conditions of the experiment were so planned that such a method of treatment is possible in this case.

COLLATED DATA CONCERNING SPEED OF REACTION.

Designation. Series and Number of Minutes.	(*a*) Rate = Bromine used in five Minutes. Milligrams.	(*b*) HBr present. Milligrams.	(*c*) Bromine present. Milligrams.	$\frac{ab}{c}$
IV 24	4.0	60	94	2.6
IV 37	3.0	71	84	2.6
IV 52	2.4	79	76	2.5
IV 95	1.52	95	58	2.5
IV 105	1.40	98	56	2.5
IV 180	0.83	115	39	2.4
IV 240	8.58	124	32	2.2
IV 360	0.25	134	18	1.9
V 30	3.5	98	124	2.7
V 89	1.7	124	98	2.1
V 123	1.3	134	87	2.0
V 180	1.0	148	74	2.0
VI 52	1.6	168	134	2.0
VI 270	0.76	213	89	1.8

It is reasonable to suppose that the effect of the hydrobromic acid will be eliminated if we compare speeds of reaction in solutions containing equal concentrations of hydrobromic acid. It is true that the cause of the retarding action of this substance may affect its available concentration, but clearly a first approximation may be reached in this way. We should expect to find the residual difference in rate to be due to the bromine alone, and hence be able to discover at once to what type the bromine reaction belongs.

It is easily seen that Series IV contained 124 milligrams of hydrobromic acid after 240 minutes, while Series V contained the same amount after only 89 minutes. Now the amounts of bromine present in these two cases were respectively 32 and 98 milligrams, while the rates were

0.58 and 1.7 respectively. These numbers are so nearly proportional as to indicate beyond question a monomolecular reaction, directly dependent upon the concentration of the bromine alone. The corresponding values of $\frac{ab}{c}$ are respectively 2.2 and 2.1, which of course express the same relation. For further evidence one may compare the values corresponding to 98 to 134 milligrams of hydrobromic acid, in each of which cases a similar equality of the "constant" is to be noted.

The simplest interpretation of this result is to ascribe to hydrobromic acid a catalytic retarding action. This would be rather a classification than an explanation, however, — for no one pretends to understand the exact mechanism of catalytic changes.

In cases like the present one, where some of the side influences are difficult to interpret, every possible means of determining the order of a reaction should be employed. The other chief methods which have been proposed are those due to van't Hoff,* who suggested calculating according to the equation of each of the orders so as to find which answers; or else studying the reaction with varying dilutions, and comparing the results; and the "isolation method," which consists in putting in so great an excess of all except one of the reacting substances that it alone changed perceptibly during the reaction. †

The present case is too complex for the first two methods; accordingly the last method was tried, but without notable success. When fifteen or twenty times as much hydrobromic acid is added to the solution as will be formed during the reaction, the speed is so repressed that in order to bring about any appreciable reaction, we were compelled to work at comparatively high temperatures. Even at 50° C. the action was exceedingly slow, and a great part of loss of bromine at this temperature was found to be due to its reaction with water according to the equation $2H_2O + 2Br_2 = O_2 + 4HBr$. It might be argued that we could have obtained the value of the speed of this last reaction, and by subtraction eliminate the error introduced by it into the apparent bromine-oxalic acid reaction. Such a course, however, would be unsafe, inasmuch as we know nothing of the mutual influence of the two reactions. Very probably the speed of reaction resulting from the action of water and oxalic acid on bromine is not equal to the sum of the speed of water on bromine plus the speed of the bromine-oxalic acid reaction. The assumption of such an equality would at all events be hazardous. Since bromine has no appreciable action on water in the dark at ordinary temperatures, this objection has no important weight when offered against the main portion of the work outlined in this paper.

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* Van't Hoff, Vorlesungen, I. p. 193 (1898).

† See Ostwald, Lehrbuch für allg. Chem., **2**, II. 238. Further information concerning these matters may be had from the papers by A. A. Noyes, Zeitschr. phys. Chem., **18**, 118 (1895), **19**, 599 (1896), also T. S. Price, ibid. **27**, 479 (1898), etc.

It becomes now a matter of importance to determine the cause of this remarkable specific action of the hydrobromic acid. That the relation is a complex one goes without saying. As has already been pointed out, the smallness of the effect caused by hydrochloric acid indicates that the depression of the dissociation of the oxalic acid is not the only cause at work. On comparing the effect of different concentrations of hydrobromic acid in the presence of like concentrations of the other substances, it is seen that the retarding effect grows faster than the concentration of the hydrobromic acid. Thus when 88 milligrams of bromine were present, 65 milligrams of hydrobromic acid allowed a rate of 3.3, while 134 depressed the rate to 1.3 (IV, 31, and V, 123). A doubling of the concentration of the hydrobromic acid more than halved the rate.

If this effect is catalytic, and peculiar to this reaction, we should expect to find different effects in other cases. On the other hand, it is possible that the hydrobromic acid may really enter into combination with some of the bromine, and thus withdraw it from the reaction. If hydrobromic acid diminishes the reacting concentration of bromine in this case, it should also produce this effect in all other cases, both chemical and physical. It should, for example, diminish the bromine-vapor tension of bromine water. This conclusion was easily tested, and found to be amply supported by fact. It forms another link in the chain of evidence indicating the existence of polybromides in solution.

When hydrobromic acid is added to an aqueous solution of bromine the color of the latter is lost to a great degree, the solution becoming much paler. Such a color change indicates chemical change. That the vapor tension is much depressed was clearly shown by the following experiment: —

Six gas-washing bottles were arranged in series, and into the first (A) was put a solution of bromine in water. The second and third bottles contained a solution of potassium iodide. Into the fourth (D) a bromine solution containing hydrobromic acid was introduced, and the last two bottles were filled with the iodine solution. The arrangement was as shown below, —

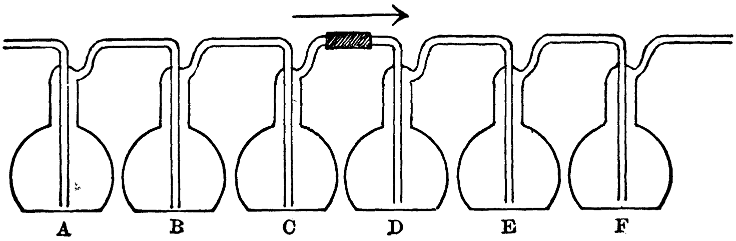

FIGURE 3.

Air was drawn through the solutions, and the liberated iodine in B and E titrated with thiosulphate. Free iodine, equivalent to 22.80 c.c. $\frac{n}{10}$ thiosulphate, was found in bottle B, while the acid solution of bromine, D, had given up to E only the equivalent of 2.50 c.c. of $\frac{n}{10}$ thiosulphate. No iodine was set free in C or F. This experiment was repeated, letting the air first pass through the bromine solution containing hydrobromic acid and then through the aqueous solution of pure bromine. The bromine containing the acid lost bromine equivalent to 2.10 c.c. of thiosulphate $\frac{n}{10}$, while the solution free from acid lost the equivalent of 21.00 c.c. The strength of the hydrobromic acid was about five per cent. It is evident from this that hydrobromic acid in some way combines with bromine. A solution of potassium bromide was found to act in the same way.

Similar results have been attained by Jakovkin * by studying the distribution of bromine between carbon disulphide and solutions of bromides. He found that even chlorides in solution possess a slight, although far less marked tendency to diminish the reacting tendency of bromine, while the effect of bromides is very great.

This effect must be due, of course, to the formation of tribromides in solution, and there is good reason to believe that these are about as highly ionized as the bromides from which they are formed. Hence the retarding action of hydrobromic acid may be supposed to be due chiefly to the tendency of the bromide ion to add bromine, and thus to remove this bromine from the field of action.

The essential details of the action of bromine on oxalic acid may therefore be supposed to take place in accordance with the following scheme, in which the main reaction under investigation is underlined.

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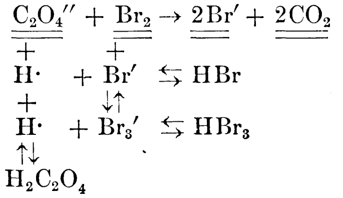
* Zeitschr. phys. Chem. **20**, 19 (1896).



$$\begin{array}{lllll}
\underline{\underline{C_2O_4''}} & + & \underline{\underline{Br_2}} & \rightarrow & \underline{\underline{2Br'}} + \underline{\underline{2CO_2}} \\
+ & & + & & \\
H^{\cdot} & + & Br' & \leftrightarrows & HBr \\
+ & & \downarrow\uparrow & & \\
H^{\cdot} & + & Br_3' & \leftrightarrows & HBr_3 \\
\uparrow\downarrow & & & & \\
H_2C_2O_4 & & & &
\end{array}$$

But how is it possible to reconcile this complex reaction with the simple mathematical expression $\frac{a\,b}{c}$ which was found to hold approximately for moderate dilutions? If we represent by $f\,a$* the concentration of the *active* bromine, by b the total concentration of the hydrobromic acid, and by c the total bromine, the requirement of "mass law" would be at least as complicated as

$$(f\,a)^{n}\left[b-\frac{n_1}{n}(c-f\,a)\right]^{n_1}=k\,(c-f\,a)^{n_2}.$$

This is on the assumption that the law holds exactly, and that the hydrogen tribromide is ionized to the same extent as the hydrobromic acid. Qualitatively this equation holds true; for an increase in c actually causes an increase in a, as the equation demands. If all the n values are assumed to be unity, it is clear that $f\,a$ must grow in greater proportion than $c-f\,a$ with increasing c and constant b. Moreover, c must grow faster than $c-f\,a$; and it is not at all impossible that for moderate concentrations the relation might be such that $\frac{f\,a}{c}=k$, — the observed approximate fact.

In view of the many-sided relationships shown by the reaction diagram, incomplete as it is, and the inaccuracy of the "law of mass-action" when applied to electrolytes, it is hardly worth while to attempt to construct any more precise mathematical relationship. That which has been pointed out, taken in connection with facts concerning other reactions and the known existence of polybromides, seems to indicate that it is not necessary to class the action of hydrobromic acid among catalytic phenomena; the reaction indicated on this page seems a more probable explanation.

SUMMARY.

The following points may be repeated as the chief outcome of the present investigation: —

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* a signifies the rate of change; the active bromine may be assumed as a function of this rate.

1. Bromine water reacts slowly upon oxalic acid at ordinary room temperatures, and rapidly at higher temperatures.

2. The concentration of the oxalic acid may be varied through wide limits without seriously changing the speed of the reaction.

3. Neutralization or the addition of salts of weaker acids immensely accelerates the reaction.

4. The addition of strong acids retards the reaction.

5. Hydrobromic acid has a retarding effect more than ten times as great as hydrochloric acid.

6. The bromine-vapor pressure of bromine water is likewise greatly diminished by the addition of hydrobromic acid or a bromide.

7. Taking all these facts into consideration, it is shown with the help of the "Law of Mass Action," and the hypothesis of electrolytic dissociation, that the main reaction under consideration is probably the following: $C_2O_4'' + Br_2 \leftrightarrows 2Br' + 2CO_2$; but that this reaction is greatly retarded, as the change progresses, by the conversion of some of the otherwise available bromine into the complex ion Br_3' by union with the bromine ion formed in the main reaction.

Cambridge, Mass, U. S. A.
June 6, 1902.